Influence of magnetic impurities on the heat capacity of nuclear spins.

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Abstract

It is found that in a wide range of temperatures and magnetic fields even a small concentration of magnetic impurities in a sample leads to a T^{-1} temperature dependence of the nuclear heat capacity. This effect is related to a nuclear-spin polarization by the magnetic impurities. The parameter that controls the theory turns out not to be the impurity concentration C_{imp} but instead the quantity $c_{imp}\mu_e/\mu_n$, where μ_e and μ_n are the magnetic moments of an electron and a nucleus, respectively. The ratio of μ_e and μ_n is of order of 10^3.

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During the last years nuclear spin ordering has been observed in a considerable number of solids. For a review see Ref. [1]. This is due to an impressive progress in cooling nuclear spin systems and temperatures as low as $T \sim 10^{-9}K$ have been attained. The ordering temperatures of the nuclear spin systems are as small as $58nK$ for Cu and $0.56nK$ for Ag [2], [3]. The Curie temperature for $AuIn_2$ is $35\mu K$. In this system an interplay between nuclear magnetism and superconductivity has been observed [4].

At such low temperatures all degrees of freedom of the solid are frozen with the exception

of the nuclear spins. The temperature dependence of the resistivity is therefore due to conduction electron-nuclear spin interactions [5]. It Ref. [6] it was demonstrated that the nuclear-spin susceptibility depends on the impurity concentration and that the heat capacity in low external magnetic fields does not obey a Schottky law. Instead, it is more close to a $1/T$ behaviour. This seems to hold for a number of compounds [6].

The aim of this paper is to show that magnetic impurities can give the main contribution to the heat capacity at low temperatures even if their concentration is very low. In the following we want to give a simple physical argument to justify that statement before we present a more quantitative theory.

Consider for simplicity a system in which the magnetic interaction between nuclear spins as well as between an impurity and the nuclear spins is of the dipolar form

$$V_{1,2} = \frac{\mu_1 \mu_{\mathbf{2}} r^2 - 3(\mu_1 \mathbf{r})(\mu_2 \mathbf{r})}{r^5}. \tag{1}$$

Here $\mu_{1,2} = \mu_{1,2}\mathbf{S}_{1,2}$, $\mu_{1,2}$ and $\mathbf{S}_{1,2}$ are the magnetic moment and spin operators of two particles $1, 2$ separated by a distance $\mathbf{r}$. The temperature of the nuclear-spin ordering is accordingly of order $T_{cn} \simeq \mu_n^2/a^3$, where a is the distance between neighbouring nuclei. Note that the density of sites, i.e., nuclei, is $n_n \simeq a^{-3}$.

The crucial point is that the interaction between the impurity spin and a nuclear spin is much larger than the one between nuclear spins since the magnetic moment μ_{imp} is much larger than the one of the nuclei μ_n, i.e., $\mu_{imp}/\mu_n \simeq 10^3$. Therefore, around each impurity there is a volume of size $a^3\mu_{imp}/\mu_n$ in which the impurity-nuclei interaction exceeds the one among the nuclei. Consequently, if the impurity concentration c_{imp} exceeds μ_n/μ_{imp} the different regions with dominating impurity-nuclei interaction overlap and influence each other. We shall consider here the clean limit, i.e., concentrations $c_{imp} < \mu_n/\mu_{imp}$. In that case it suffices to consider a single impurity. The calculated contribution to the heat capacity has then to be multiplied merely by c_{imp}. Furthermore, we shall assume that the impurity spin is kept fixed by an applied magnetic field H_0, i.e., $\mu_{imp}H_0 \gg T_e$, where T_e denotes the temperature of the electron system. For $T_e \simeq 10^{-4}K$ this requires a magnetic field of order 1

Gauss. In $AuIn_2$ [4] the electron-nuclei interaction is sufficiently strong so that the nuclear temperature T and the electron temperature T_e coincide. The effective field $\mathbf{H}$ acting on a nucleus consists then of the external field $\mathbf{H}_0$ and the field set up by the impurity, i.e.,

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{H}_1 \tag{2}$$

$$\mathbf{H}_1(\mathbf{r}_n) = \frac{3(\mu_{imp}\mathbf{r})\mathbf{r}/r^2 - \mu_{imp}}{r^3}. \tag{3}$$

Here $\mathbf{r} = \mathbf{r}_n - \mathbf{r}_{imp}$ is the distance between nucleus and impurity. The interaction Hamiltonian is $H_{int} = -(\mu_n \mathbf{H})$. The partition function Z_n of a nuclear spin is

$$Z_n = \frac{sinh(\chi(2S+1))}{sinh(\chi)},\ \chi = \frac{\mu_n H(r)}{2T}, \tag{4}$$

where S is the spin of the nucleus.

The specific heat contribution follows from $C_n = -T\frac{\partial^2 F_n}{\partial T^2}$ where $F_n = -T \ln Z_n$. Here we have set Boltzmann's constant $k_B = 1$. This gives

$$C_n = \chi^2(\frac{1}{sinh^2\chi} - \frac{(2S+1)^2}{sinh^2(\chi(2S+1))}). \tag{5}$$

The average value of the specific heat $\bar{C_n}$ is a sum over $\mathbf{r}_n$ multiplied by the impurity concentration. Furthermore, it is advantageous to subtract the specific heat $C_n^{(0)}$ of the pure material

$$\bar{C_n} - C_n^{(0)} = n_{imp} \sum_{\mathbf{r}_n} (C_n(H(\mathbf{r}_n)) - C_n^{(0}(H_0)) \tag{6}$$

When $C_n^{(0)}$ is expanded in powers of $\mu_n H_0/T$ we obtain to leading order in the external field

$$C_n^0 = n_n(\frac{\mu_n H_0}{T})^2 \frac{S(S+1)}{3} \tag{7}$$

Where n_n is the concentration of nuclei.

In order that a high-temperature expansion of this type does also hold for the nuclei close to the impurity the condition $T \gg \mu_{imp}\mu_n/a^3$ must be fulfilled. The square of the effective field is

$$H^2(\mathbf{r}) = H_0^2 + \frac{3(\mu_{imp}\mathbf{r})^2 - \mu_{imp}^2 r^2}{r^8} + \frac{2}{r^5}(3(\mathbf{r}\mathbf{H}_0)(\mu_{imp}\mathbf{r}) - (\mu_{imp}\mathbf{H}_0)r^2) \tag{8}$$

From Eqs. (6-8) the following expression is obtained for the specific heat in the high-temperature regime,

$$\bar{C_n} - C_n^{(0)} = n_{imp}\frac{\mu_n^2}{T^2}\frac{S(S+1)}{3}\sum_{\mathbf{r}_n}\frac{3(\mu_{imp}\mathbf{r})^2 + \mu_{imp}^2 r^2}{r^8}. \tag{9}$$

The sum converges very rapidly. For fields less than

$$H_{00} = \frac{\mu_{imp}}{a^3}(n_{imp})^{1/2} \tag{10}$$

the main contribution to the specific heat comes from nuclei close to the magnetic impurity.

Consider next the range in T and H_0 defined by the inequalities

$$\mu H_0 \ll T \tag{11}$$

$$\frac{\mu_n\mu_{imp}}{a^3} \gg T \gg T_{cn}(=\frac{\mu_n^2}{a^3}). \tag{12}$$

In that region the main contribution to the specific heat comes from nuclei at large distance from the impurity, i.e., $r \gg a$. For them one needs not accounting for the spin-spin interaction between nuclei (see Eq. (11)) and one can also convert the summation over $\mathbf{r}_n$ into an integral of the form $n_n \int d^3\mathbf{r}...$. From Eq. (6) we obtain in this case

$$\bar{C_n} - C_n^{(0)} = n_{imp}\frac{4\pi n_n\mu_{imp}\mu_n S}{3T}(1 + \frac{1}{2\cdot 3^{1/2}}ln(2+3^{1/2})) \tag{13}$$

By comparing Eqs. (7) and (13) one notices that for fields

$$H_0 < (\frac{\mu_{imp}Tn_{imp}}{\mu_n})^{1/2} \tag{14}$$

the main contribution to the specific heat of the nuclear spin system comes from the interaction with magnetic impurities. The temperature dependence of this contribution is T^{-1} rather then T^{-2}. A dependence of this kind was indeed observed in Ref. [6] for $AuIn_2$. We suggest that it is due to the impurity effect discussed here. However, for a quantitative comparison one must take into account that the main contribution to the specific heat comes

from the In nuclei which have spin $S = 9/2$. The electric-field gradient due to the impurity leads to a quadrupolar splitting of the spin levels. Being proportional to r^{-3} the electric-field gradient leads also to a T^{-1} temperature dependence of the specific heat. For metals with nuclear spin $S = 1/2$ like Ag [2] a quadrupolar splitting does, of course, not occur.

A T^{-1} contribution results also from the nuclear spin-impurity spin RKKY-type of interaction V_R

$$V_R = -\frac{\mu_n \mu_{\mathbf{imp}}}{r^3} \chi f(2p_F r) \; ; f(x) = cos(x) - \frac{sin(x)}{x}. \tag{15}$$

Here χ is a parameter proportional to the spin-spin Fermi contact interaction [7]. This interaction is proportional to the electronic charge at the nucleus of the impurity [8]. For a light nucleus $\chi \ll 1$, while for a heavy one $\chi \gg 1$. Therefore in a metal the spin-spin interactions between the nucleus of an impurity and the ones of the host contain two contributions given by Eqs. (1,15). As pointed out before, we shall consider here only the universal dipole-dipole interaction (1), which is the same in metals and insulators.

Next we consider the case of a strong magnetic field $\mu_n H_0 \gg T$. In this regime the heat capacity is exponentially small (see Eq. (5)). The main contribution to it originates from nuclei for which the effective field $H(\mathbf{r})$ is of order T/μ_n. From Eq. (8) we find

$$H^2 = (\frac{\mu_{imp}}{r^3} - H_0)^2 + \frac{3\mu_{imp}}{r^3}(\frac{\mu_{imp}}{r^3} + 2H_0)\frac{(\mathbf{H}_0\mathbf{r})}{H_0 r}. \tag{16}$$

One notices that $H(\mathbf{r})$ is zero along a circle of radius $r_0 = (\mu_{imp}/H_0)^{1/3}$ around the impurity in a plane perpendicular to $\mathbf{H}_0$. The nuclei contributing most to the specific heat are within a torus with its axis given by the circle of radius r_0. If δr denotes the distance from this axis and if $z = (\mathbf{H}_0\mathbf{r})/H_0 r$ we find for the effective field

$$H^2 = 9H_0^2(z^2 + (\delta r/r_0)^2). \tag{17}$$

With the help of Eqs. (5,17) we obtain

$$\bar{C_n} - C_n^{(0)} = \frac{16\pi^2 T^2 \mu_{imp} n_n n_{imp}}{9H_0^3 \mu_n^2}(1 - \frac{1}{(2S+1)^2})I_1 \tag{18}$$

where

$$I_1 = \int_0^\infty \frac{dx\ x^3}{sinh^2 x} = \frac{3}{2}\zeta(3), \tag{19}$$

and $\zeta(x)$ is Riemann's zeta function.

Replacing the sum over $\mathbf{r}_n$ by an integral $n_n \int d^3\mathbf{r}$ is justified only if many nuclei are placed within a radius $\delta r/r_0 \simeq z \simeq T/(\mu_n H_0)$ of the torus. This restriction leads to the requirement

$$\frac{T^2 \mu_{imp} \mu_n n_n}{(\mu_n H_0)^3} \gg 1 \tag{20}$$

in order for Eq. (18) to hold. Together with the starting assumption ($\mu_n H_0 \gg T$) this implies the condition

$$T \ll \mu_n H_0 \ll (T^2 \mu_{imp} \mu_n n_n)^{1/3} \tag{21}$$

on the applied field H_0.

Next we deal with the case that the impurity spins are frozen in a glassy state. Then Eqs. (5,6) must be averaged over all directions of the external field $\mathbf{H}_0$. As stated before, the main contribution to the nuclear heat capacity comes from nuclei in an effective field $H \simeq T/\mu_n$. As a result we obtain

$$\bar{C_n} - C_n^{(0)} = \frac{32\pi T^3 \mu_{imp} n_n n_{imp}}{3 H_0^4 \mu_n^3} (1 + \frac{1}{2\sqrt{3}} ln(2+\sqrt{3}))(1 - \frac{1}{(2S+1)^3}) I_2, \tag{22}$$

where

$$I_2 = \int_0^\infty \frac{dx\ x^4}{sinh^2 x} = \frac{\pi^4}{30}. \tag{23}$$

The restriction (21) for H_0 is changed accordingly into

$$T \ll \mu_n H_0 \ll (T^3 \mu_{imp} \mu_n n_n)^{1/4}. \tag{24}$$

The required range of strong magnetic fields has not yet been studied experimentally, although in Ref. [6] the region $\mu_n H_0 \leq T$ was investigated. For metals in the clean limit the

nuclear-spin contribution to the heat capacity has a maximum near $\mu_n H_0 \sim T$, the position of which is only weakly dependent on the magnetic impurity concentration n_{imp}, provided $n_{imp}\mu_{imp}/\mu_n \ll n_n$. We expect that in the strong-field regime $\mu_n H_0 \gg T$ the heat capacity has a power-law behaviour given by Eqs. (18) and (22). For pure samples an exponential temperature dependence is obtained (see Eq. (5)).

In summary, we have shown that in a wide region of temperature and magnetic fields the main contribution to the nuclear specific heat results from their interaction with small amounts of magnetic impurities which are present in most of the systems.

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